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(54) HONEYCOMB STRUCTURE AND PRODUCTION METHOD THEREFOR

(57)Abstract:
PROBLEM TO BE SOLVED: To provide a honeycomb structure which can inexpensively be produced at a relatively low burning temperature while containing refractory particles such as silicon carbide particles, is sufficiently porous, also has a high specific surface area, and is suitable usable even under a high SV(space velocity) condition, e.g. as a filter and a catalytic carrier for purifying automobile exhaust gas.
SOLUTION: The honeycomb structure has many circulation pores partitioned by bulkheads and piercing in the axial direction. The honeycomb structure contains refractory particles as aggregates and one or more kinds of elements selected from the groups consisting of rare earth metals, alkaline earth metals, Al and Si. The honeycomb structure has crystals containing one or more kinds selected from the above elements, and is porous.

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CLAIMS

[Claim(s)]
[Claim 1] The honeycomb structure object which has a crystal containing one or more sorts of these elements including the fireproof particle which is the honeycomb structure object which has the circulation hole of a large number penetrated to the shaft orientations divided by the septum, and serves as the aggregate, and rare earth, an alkaline earth and one or more sorts of elements chosen from the group which consists of aluminum and Si, and is characterized by being porosity.
[Claim 2] Furthermore, the honeycomb structure object containing B and/or C according to claim 1.
[Claim 3] The honeycomb structure object according to claim 1 which has the structure combined with said crystal after said fireproof particle had stopped the raw material particle shape.
[Claim 4] The honeycomb structure object according to claim 1 said whose fireproof particle is a silicon carbide particle.
[Claim 5] The honeycomb structure object according to claim 1 used as a filter which carries out uptake removal of the particulate matter contained in dust-containing fluid.
[Claim 6] The honeycomb structure object according to claim 1 in the range whose porosity is 30 - 90%.
[Claim 7] The honeycomb structure object according to claim 1 in the range whose average pore size is 2-50 micrometers.
[Claim 8] The honeycomb structure object according to claim 1 whose thickness of said septum is 102-1270 micrometers.
[Claim 9] The honeycomb structure object according to claim 1 with which the thickness of said septum and the porosity of a honeycomb structure object fill the following relation.
[Equation 1] thickness (micrometer) >= porosity (%) x4 of a septum -- [Claim 10] The honeycomb structure object according to claim 1 with which the thickness of said septum and the porosity of a honeycomb structure object fill the following relation.
[Equation 2] thickness (micrometer) >= porosity (%) x5 of a septum -- [Claim 11] The honeycomb structure object according to claim 1 with which the thickness of said septum and the porosity of a honeycomb structure object fill the following relation.
[Equation 3] thickness (micrometer) <= porosity (%) x20 of a septum -- [Claim 12] The honeycomb structure object according to claim 1 whose cel consistencies are 0.7 - 155 cel / cm2.
[Claim 13] The manufacture approach of the honeycomb structure object characterize by to carry out actual baking after adding one or more sorts of the raw materials and the organic binders containing one or more sorts of elements chose from the group which become a fireproof particle raw material from rare earth , an alkaline earth , and aluminum and Si , fabricating the plastic matter mix , and knead and obtained in a honeycomb configuration , carrying out temporary quenching of the acquired Plastic solid and removing the organic binder in a Plastic solid .
[Claim 14] The manufacture approach according to claim 13 that said fireproof particle raw material is a silicon carbide particle raw material.
[Claim 15] The manufacture approach according to claim 13 that the mean particle diameter of said fireproof particle raw material is 2 to 4 times the average pore size of the honeycomb structure object finally acquired.
[Claim 16] The manufacture approach according to claim 13 that the addition of one or more sorts of raw materials containing said rare earth, an alkaline earth, and one or more sorts of elements chosen from the group which consists of aluminum and Si is 3 - 30 g/m2 to the surface area of a fireproof particle.
[Claim 17] The manufacture approach according to claim 13 that the mean particle diameter of one or more sorts of raw materials containing said alkaline earth and one or more sorts of elements chosen from the group which consists of aluminum and Si is 50% or less of the mean particle diameter of the fireproof

particle which is the aggregate.
[Claim 18] The manufacture approach according to claim 13 added in 2 - 30% of the weight of the range by outside ** to the total quantity with one or more sorts of raw materials containing one or more sorts of elements chosen from the group which consists said organic binder of said fireproof particle raw material and rare earth, an alkaline earth, and aluminum and Si.
[Claim 19] The manufacture approach according to claim 13 added in 30 or less % of the weight of the range by outside ** to the total quantity with one or more sorts of raw materials which contained one or more sorts of elements chosen from the group which consists an ostomy agent of said fireproof particle raw material and rare earth, an alkaline earth, and aluminum and Si when preparing said plastic matter.
[Claim 20] The manufacture approach according to claim 13 which adds the raw material which contains B and/or C in said fireproof particle raw material further in case said plastic matter is prepared.
[Claim 21] The manufacture approach according to claim 13 which adds the element more than tetravalence as a nucleation agent further in said fireproof particle raw material in case said plastic matter is prepared.
[Claim 22] The manufacture approach according to claim 13 enforced at temperature lower than the temperature which one or more sorts of raw materials containing one or more sorts of elements chosen from the group which consists temporary quenching of said Plastic solid of said rare earth, an alkaline earth, and aluminum and Si fuse.
[Claim 23] The manufacture approach according to claim 13 of carrying out said this baking in a 1500-2000-degree C temperature requirement.
[Claim 24] The manufacture approach according to claim 13 of establishing the annealing process for crystallization held at the temperature of 1500 degrees C or less in said this baking after holding with the highest burning temperature.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to the honeycomb structure object used for a filter, catalyst support, etc. for automobile exhaust purification.
[0002]
[Description of the Prior Art] The porous honeycomb structure object is widely used as catalyst support for supporting the catalyst component which purifies the filter for carrying out uptake removal of the particulate matter contained in dust-containing fluid like diesel-power-plant exhaust gas, or the harmful matter in exhaust gas. Moreover, using a fireproof particle like a silicon carbide (SiC) particle as a component of such a honeycomb structure object is known.
[0003] As a concrete related technique, the silicon carbide powder which has a predetermined specific surface area and a predetermined impurity content is used as a start raw material, and the nature catalyst support of porosity silicon carbide of the honeycomb structure calcinated and acquired by the configuration of a request of this after shaping and desiccation in a 1600-2200-degree C temperature requirement is indicated by JP,6-182228,A.
[0004] A vitrification material adds to the fireproof constituent which, on the other hand, contains an easy-oxidizable material or an easy-oxidizable material in JP,61-26550,A, and the silicon-carbide Plastic solid with which the manufacture approach of the vitrification material content refractories characterized by to carry out nakedness baking of the Plastic solid mixed, kneaded, and fabricated and fabricated in the furnace of a non-oxidizing atmosphere adds and fabricates an organic binder and the inorganic binder of a clay mineral system, textile glass yarn, and a silicic-acid lithium system to silicon-carbide powder at JP,8-165171,A is indicated with binding material, respectively.
[0005] Moreover, after adding and fabricating binding material, such as glassiness flux or argillaceous, to the silicon carbide particle used as the aggregate as the manufacture approach of the conventional nature sintered compact of porosity silicon carbide, the method of burning, hardening and manufacturing the Plastic solid at the temperature which said binding material fuses is also introduced to said JP,6-182228,A.
[0006] furthermore, to JP,61-13845,B and JP,61-13846,B Silica sand, a pottery grinding object, aluminum2O3, TiO2, the metallic oxide of ZrO2 grade, The fireproof particle by which the particle size regulation was carried out to the predetermined grain size which consists of silicon carbide, a nitride, boride, or other fireproof ingredients The suitable fireproof particle pitch diameter, fireproof particle particle size distribution, tube-like object porosity, tube-like object average pore size, tube-like object pore volume, tube-like object septum thickness, etc. are indicated about the high-temperature-service ceramic filter formed in the porous cylinder-like-object-with-base-like object with fireproof binding material, such as water glass, a frit, and a cover coat.
[0007] Furthermore, the manufacture approach of the silicon carbide brick combined by the sialon which is the acid nitride of Si and aluminum, the presentation, etc. are indicated by JP,10-29866,A, JP,2-6371,A, and JP,61-97165,A again.
[0008]
[Problem(s) to be Solved by the Invention] Although a silicon carbide component evaporates from a silicon carbide particle front face, the neck section grows because this condenses in the contact section between particles (neck section), and an integrated state is obtained with the sintering gestalt (necking) by the recrystallization reaction of the silicon carbide powder itself shown in said JP,6-182228,A In order for this to have to cause cost quantity since a very high burning temperature is required, and to evaporate silicon carbide and to have to carry out elevated-temperature baking of the ingredient with a high coefficient of

thermal expansion, there was a problem that a baking yield fell.
[0009] Although the technique of on the other hand combining the coal-for-coke-making-ized silicon powder shown in JP,61-26550,A or JP,6-182228,A by glassiness was low and ended with 1000-1400 degrees C as a burning temperature, since binding material will once be in a melting condition at this time, it was very difficult to obtain a porous body.
[0010] Furthermore, although the filter shown in JP,61-13845,B and JP,61-13846,B was porosity, septa are 5-20mm and a thick cylinder-like-object-with-base-like object, and were not able to apply it to the bottom of a high SV (space velocity) condition like the filter for automobile exhaust purification.
[0011] Furthermore, when each silicon carbide brick combined again by the sialon shown in JP,10-29866,A, JP,2-6371,A, and JP,61-97165,A is used for lining of a furnace, a shelf board, etc., its porosity was as small as 20% or less and pressure loss was taken into consideration, it was what is not suitable for an application like the filter for automobile exhaust purification at all.
[0012] This invention is fully porosity and high specific surface area, and aims at offering the honeycomb structure object which can be suitably used also under high SV conditions as the filter for automobile exhaust purification, or catalyst support by processing of ****** etc., and its manufacture approach while being able to manufacture them cheaply with a comparatively low burning temperature, though it is made in view of such a conventional situation and a fireproof particle like a silicon carbide particle is included.
[0013]
[Means for Solving the Problem] It is the honeycomb structure object which has the circulation hole of a large number which are penetrated to the shaft orientations divided by the septum according to this invention, and it has a crystal containing one or more sorts of these elements including the fireproof particle used as the aggregate, and rare earth, an alkaline earth and one or more sorts of elements chosen from the group which consists of aluminum and Si, and honeycomb structure object ** characterized by being porosity is offered.
[0014] According to this invention, in a fireproof particle raw material Moreover, rare earth, an alkaline earth, Add one or more sorts of the raw materials and the organic binders containing one or more sorts of elements chosen from the group which consists of aluminum and Si, and the plastic matter mixed, and kneaded and obtained is fabricated in a honeycomb configuration. After carrying out temporary quenching of the acquired Plastic solid and removing the organic binder in a Plastic solid, manufacture approach ** of the honeycomb structure object characterized by carrying out actual baking is offered.
[0015]
[Embodiment of the Invention] The honeycomb structure object of this invention combines fireproof particles using the device of a dissolution deposit to the manufacture approach indicated by said JP,6-182228,A, for example using the device of evaporation condensation in a sintering-machine style. By this dissolution deposit device, suitable sintering acid is chosen, if it adds, mixes and calcinates to the fireproof particle which is the aggregate, that assistant will react with a fireproof particle, the front face of a fireproof particle will dissolve in that case, and the liquid phase will be generated. While the component of the added assistant had been included, the component which dissolved moves to the low neck section of an energy state in the state of the liquid phase, and deposits, and the matter which moved to the neck section combines particles.
[0016] If assistants react first in a baking process, the liquid phase may be generated and it may react with a fireproof particle, the reaction of an assistant and a fireproof particle may generate the liquid phase. However, since the direction of the condition of the liquid phase tends to get wet to a fireproof particle and a reaction generally becomes easy, it is desirable to choose the combination about which assistants have the eutectic point lower than burning temperature. Specifically, rare earth (Y, La, Ce, Yb, etc.), alkaline earths (Mg, calcium, Sr, Ba, etc.), and one or more sorts of raw materials (henceforth "content raw materials, such as rare earth,") containing one or more sorts of elements chosen from the group which consists of aluminum and Si are used as an assistant. Also among said elements, especially Si is effective for lowering the melting point of an assistant.
[0017] One or more sorts of elements which are contained in the honeycomb structure object of this invention and which were chosen from rare earth, alkalinity, and the group that consists of aluminum and Si are contained in the raw material added as an assistant at the time of the manufacture in this way, are contained into the crystal which mainly deposited in the neck section, and exist in the structure. Furthermore, the raw material which contains B and/or C in a fireproof particle as an element which promotes the mass transfer on the front face of a particle, for example, B4C which is these compounds, may be added, and B and/or C will also be contained in the honeycomb structure object acquired in this case.

[0018] Moreover, although the honeycomb structure object of this invention has a crystal containing one or more sorts of aforementioned elements contained in the raw material added as an assistant, it means that the crystal deposited from this, i.e., the liquid phase. if the liquid phase is used for association of the fireproof particle which serves as the aggregate as mentioned above at all and a crystal does not deposit from the liquid phase -- baking -- although it will remain as glass inside of the body, since the reinforcement in the neck section of a fireproof particle, corrosion resistance, and thermal resistance become less enough when glass becomes the main phase of the neck section, the property of the honeycomb structure object itself will fall. For this reason, the crystal needs to deposit from the liquid phase.
[0019] As mentioned above, it does not evaporate the fireproof particle itself like the recrystallizing method, and since the fireproof particle is combined using the liquid phase generated in connection with a reaction and this, the honeycomb structure object of this invention is set at the time of the baking, does not need not much high temperature, but it can raise a yield while it holds down a manufacturing cost. Moreover, also with the cylinder-like-object-with-base-like object of a thick wall as shown in JP,61-13845,B or JP,61-13846,B, this invention is not the brick [like] shown in JP,10-29866,A, JP,2-6371,A, and JP,61-97165,A, either, and since it is a porous honeycomb structure object, it can be used under high SV conditions as a filter, catalyst support, etc. for automobile exhaust purification.
[0020] As for the honeycomb structure object of this invention, it is desirable to have the structure combined with a crystal as the microstructure after the fireproof particle had stopped the raw material particle shape. Moreover, when using the particulate matter contained in dust-containing fluid in the honeycomb structure object of this invention as a filter for carrying out uptake removal, it is desirable to make the porosity into 30 - 90% of range. If the porosity of a honeycomb structure object runs short of filtration velocity at less than 30% and exceeds 90%, the reinforcement as the structure runs short. Furthermore, when using for the application for which we are anxious about the pressure loss of the filter for automobile exhaust purification etc., it is desirable to make porosity into 40% or more.
[0021] When using the honeycomb structure object of this invention as a filter similarly, as for the average pore size of a honeycomb structure object, determining according to the object to filter is desirable. For example, when using as a diesel particulate filter (DPF) for carrying out uptake removal of the particulate contained in the exhaust gas discharged from a diesel power plant, it is desirable to make average pore size into the range of 2-50 micrometers. if a pressure loss goes up remarkably and average pore size exceeds 50 micrometers conversely also by little deposition of a particulate [pore size / average] in less than 2 micrometers -- particulate base -- since an omission happens, it is not desirable.
[0022] As for the thickness of the septum with which the circulation hole (cel) of a honeycomb structure object is divided, it is desirable to be referred to as 4 or more (102 micrometers or more) mil. It becomes difficult for the thickness of a septum to maintain reinforcement sufficient as the structure by under 4mil (102 micrometers). Moreover, reinforcement had porosity and a close relation, when in the case of the honeycomb structure object of this invention setting up the thickness of a septum so that the thickness and the porosity of a septum might fill the following relation, required reinforcement was obtained, and the desirable thing became clear.
[Equation 4] Thickness (micrometer) >= porosity (%) x4[0023] of a septum Furthermore, if the thickness of a septum is set up so that the thickness and the porosity of a septum may fill the following relation, since sufficient reinforcement will be obtained, it is more desirable.
[Equation 5] Thickness (micrometer) >= porosity (%) x5[0024] of a septum On the other hand, when using as filters, such as DPF, it is desirable to set thickness of a septum to 50 or less (1270 micrometers or less) mil. When the thickness of a septum exceeds 50mil (1270 micrometers), it is for being anxious about the lack of filtration velocity, or a pressure drop buildup. In addition, there is close relation to porosity also about this, and a problem can be avoided by setting up the thickness of a septum so that the thickness and the porosity of a septum may fill the following relation.
[Equation 6] Thickness (micrometer) <= porosity (%) x20[0025] of a septum As for the cel consistency of a honeycomb structure object, it is desirable to consider as the range of 5-1000 cel / square inch (0.7 - 155 cel / cm2). a cel consistency -- 5 cels / square -- under in an inch (0.7 cels / cm2), while becoming insufficient [reinforcement] as a honeycomb structure object, when it uses as a filter, filtration areas also run short. On the contrary, it is not desirable in order to cause a pressure drop buildup, if 1000 cel / square inch (155 cels / cm2) is exceeded.
[0026] Next, the manufacture approach of the honeycomb structure object of this invention is explained. In manufacturing the honeycomb structure object of this invention, first, content raw materials, such as rare earth, and an organic binder are added in a fireproof particle raw material, it mixes and kneads in it, and the

plastic matter for shaping is obtained.
[0027] although especially the class of fireproof particle to be used is not limited -- an oxide system -- aluminum2 -- O3, ZrO2, Y2O3, and a carbide system -- SiC and a nitride system -- Si3 -- thermal resistance of SiC is high for applications, such as DPF often exposed to an elevated temperature in case combustion processing of the particulate which particles, such as N4, AlN, and other mullites, were suitably used, for example, was accumulated is carried out, and it is suitably used for them.
[0028] As for the mean particle diameter of a fireproof particle raw material, it is desirable that it is 2 to 4 times the average pore size of the honeycomb structure object (sintered compact) finally acquired by this manufacture approach. Since the honeycomb structure object acquired by this manufacture approach has a comparatively low burning temperature, the particle shape and particle size of a fireproof particle raw material are maintained in general until after baking. Therefore, particle size is too small to desired pore size in said ratio being under 2 double, and it is difficult that it will be combined long and slender as the crystal as which the fireproof small particle group deposited as a result, big pore will be formed and the structure of a thin wall like a honeycomb structure object can be maintained to obtain such high reinforcement.
[0029] Moreover, for example, the recrystallization SiC conventionally applied to the porosity honeycomb structure object when a fireproof particle is a SiC particle The SiC particle combined with the crystal which deposited from the reaction mechanism like the honeycomb structure object of this invention to needing an aggregate raw material particle size almost equivalent to the pore size considered as a request Since **** [particle size / twice / more than / the pore size], when it is going to obtain the same pore size, compared with Recrystallization SiC, a cheap raw material can be used coarsely, and a cost merit is also large.
[0030] On the contrary, when said ratio exceeds 4 times, the particle size of the fireproof particle used to desired pore size is too large, and it is not desirable by being densely filled up with a fireproof particle in the phase of shaping at the point which becomes difficult [it / to obtain desired pore] for the gap, and causes a porosity fall for a filter application further.
[0031] Content raw materials, such as rare earth, react with a fireproof particle during baking, or react from the raw materials concerned, and generate the liquid phase, and since they bear the role to which it coils around a fireproof particle and joins particles, the suitable addition has the close relation with the surface area of a fireproof particle. although the surface area of the fireproof particle in this case is based on the configuration of a particle etc. since the liquid phase is the translation which is arguing that a fireproof particle is covered and it pastes up, generally it is [particle / fireproof] and wholly more nearly geometric in a solid sphere than the so-called BET specific surface area the bottom rather -- it is more suitable to use surface area S=4pir2 (for r to be the mean particle diameter of a fireproof particle). this -- geometric -- if surface area S=4pir2 are used, "the amount W of content raw materials, such as rare earth per fireproof particle unit surface area," is computable in simple by the bottom formula.
[Equation 7] W= {(4/3pir3xrho) /(weight rate of a fireproof particle)} x {(weight rate of content raw materials, such as rare earth) /(4pir2)} (here, r is the mean particle diameter of a fireproof particle, and rho is the specific gravity of a fireproof particle.)
[0032] As for the addition of content raw materials, such as rare earth, in the manufacture approach of this invention, it is desirable to set up so that "the amount W of content raw materials, such as rare earth per fireproof particle unit surface area," may be set to 3-30g/m2. Since the liquid phase will be superfluously generated more than it can combine fireproof particles appropriately if it is difficult for binding material to be insufficient and to obtain the reinforcement which can maintain the structure of a thin wall like honeycomb structure in less than two 3 g/m and it exceeds 30 g/m2 conversely, although reinforcement improves, evils, such as a porosity fall and average pore size contraction, occur at the same time.
[0033] As for the mean particle diameter of content raw materials, such as rare earth, it is desirable that it is 50% or less of the mean particle diameter of the fireproof particle which is the aggregate. If the particle size exceeds 50% of the particle size of a fireproof particle in order to move generating the liquid phase and gathering by baking so that it may coil around a fireproof particle, at the time of shaping, the space which the particle of content raw materials, such as rare earth, occupied serves as a big opening, content raw materials, such as rare earth, remain, a fall on the strength is caused, or when using it as a filter, they will cause filter degradation (leakage in filtration).
[0034] Moreover, it is desirable for the direction which generally mixes two or more sorts of raw material powder which has a grain-size difference to some extent at the time of extrusion molding of a honeycomb structure object to be able to extrude smoothly, and to make mean particle diameter of content raw materials, such as rare earth, into 30% or less of the mean particle diameter of the fireproof particle which is the aggregate from the viewpoint. As a raw material gestalt of content raw materials, such as rare earth,

although an oxide is used, a nitrate, mineral salt like a chloride, a nitride, a metal, etc. can usually be used as occasion demands. Moreover, if the compound containing two or more sorts in essential elements, for example, a clay mineral etc., is used, it will become advantageous in respect of cost, improvement in the productivity by improving a moldability, etc.

[0035] In order to use a fireproof particle as the aggregate and to carry out extrusion molding of the plastic matter which comes to blend an ostomy agent etc. content raw materials, such as rare earth, and if needed to a honeycomb configuration smoothly, it is desirable to add one or more sorts of organic binders 2% of the weight or more by outside ** as a shaping assistant to the total quantity of the main raw material (a fireproof particle raw material and content raw materials, such as rare earth). However, in order that the addition exceeding 30 % of the weight may cause superfluous high porosity and may make the lack of on the strength result after temporary quenching, it is not desirable.

[0036] Furthermore, when the thickness of a septum carries out extrusion molding to the honeycomb structure object below 20mil (508 micrometers), it is desirable to add an organic binder in 4 - 20% of the weight of the range. an addition -- less than 4 % of the weight -- ** -- if it is difficult to extrude in a thin wall [like] and it exceeds 20 % of the weight conversely, it will become difficult to maintain the configuration after extrusion.

[0037] When using a honeycomb structure object as a filter, an ostomy agent may be added at the time of preparation of a plastic matter in order to raise porosity. As for the addition of an ostomy agent, it is desirable to consider as 30 or less % of the weight by outside ** to the total quantity of the main raw material (a fireproof particle raw material and content raw materials, such as rare earth). If an addition exceeds 30 % of the weight, porosity will become high too much and it will result in the lack of on the strength. Since pore is formed in the marks from which it burned and escaped, as for an ostomy agent, it is desirable that it is 25 - 100% of range to the average pore size which it is going to obtain after the mean particle diameter's calcinating. As an ostomy agent to be used, graphite, wheat flour, starch, phenol resin, a polymethyl methacrylate, polyethylene, polyethylene terephthalate, etc. can be mentioned, for example. An ostomy agent may use one sort independently according to the purpose, and may use it combining two or more sorts.

[0038] Moreover, in order to promote this crystallization, you may make it add the elements more than tetravalence (Zr, Ta, Ti, P, etc.) as a nucleation agent in a fireproof particle raw material in the manufacture approach of this invention, although a crystal needs to deposit from the liquid phase as mentioned above. Furthermore, the raw material which contains in a fireproof particle raw material B and/or C which are the element which promotes the mass transfer on the front face of a particle again may be added.

[0039] Said raw material is fabricated in the honeycomb configuration of a request of the plastic matter mixed, and kneaded and obtained by the conventional method by an extrusion method etc. Subsequently, this baking is performed after removing the organic binder which carries out temporary quenching of the acquired Plastic solid, and is contained in a Plastic solid (cleaning). As for temporary quenching, it is desirable to carry out at temperature lower than the temperature which content raw materials, such as rare earth, fuse. You may once hold at the predetermined temperature of about 150-700 degrees C, and to below 50 degrees C / hr, a programming rate may be made late and, specifically, may carry out temporary quenching in a predetermined temperature region.

[0040] About the technique once held at predetermined temperature, with the class and amount of an organic binder which were used, maintenance or maintenance with the two or more temperature level of only a 1 temperature level is sufficient, and in holding with the two or more temperature level further, even if the same, you may change the holding time mutually. Moreover, between a certain 1 temperature-province regions may be similarly made late about the technique of making a programming rate late, or you may make it late among the two or more division, and, in between the two or more [further] division, a rate may be mutually changed also as the same.

[0041] Although an oxidizing atmosphere is sufficient, in order that it etc. may burn violently with oxygen and may make Plastic solid temperature rise rapidly during temporary quenching about the ambient atmosphere of temporary quenching when many organic binders are contained in a Plastic solid, it is also desirable technique by carrying out by inert atmospheres, such as N2 and Ar, to control the abnormality temperature up of a Plastic solid. Control of this abnormality temperature up is important control when a raw material with a large (weak to a thermal shock) coefficient of thermal expansion is used. It is desirable to carry out temporary quenching of the organic binder in said inert atmosphere, when it adds more than 20 % of the weight (outside **) for example, to the main raw material.

[0042] The furnace of identitas or another individual may perform this baking following temporary

quenching and it as another process, and it is good also as a continuous process in the same furnace. When carrying out temporary quenching and this baking in a different ambient atmosphere, the former is desirable technique, and from standpoints, such as the total firing time and operation cost of a furnace, the latter technique is also desirable.

[0043] Although the temperature of this baking changes with content raw materials, such as rare earth to be used, it is desirable to usually carry out in 1500-2000 degrees C. Since the bias of fireproof particles not being firmly combined since the liquid phase is not fully generated, but the viscosity of the component which dissolved when it exceeded 1600 degrees C conversely falling too much at less than 1500 degrees C, and concentrating on the baking object lower part near the baking body surface arises, the operation temperature of this baking is not desirable. In addition, in this baking of this, it is the purpose which promotes crystallization, and after holding to a maximum temperature, it is desirable to establish the annealing process for crystallization held at the temperature of 1500 degrees C or less.

[0044] Moreover, although choosing according to the class of fireproof particle is desirable about the ambient atmosphere of this baking, for example, baking by the oxidizing atmosphere is also possible when a fireproof particle has oxidation resistance the particle of carbide including SiC, and Si3 -- the particle of the nitride represented by N4 and AlN of considering as non-oxidizing atmospheres, such as N2 and Ar, etc. is desirable in the temperature region beyond the temperature from which oxidation begins at least about what is anxious about the oxidation in an elevated temperature. In addition, since a good property may be acquired rather than the crystal phase of binding material becomes a nitride and an acid nitride and uses a crystal phase as an oxide in reinforcement or thermal conductivity when calcinating in N2 ambient atmosphere, it is also desirable to use a firing environments properly according to the purpose.

[0045]

[Example] Hereafter, although this invention is further explained to a detail based on an example, this invention is not limited to these examples.

[0046] The SiC raw material powder which has mean particle diameter as shown in Table 1, (Examples 1-7) 2OY3 powder with a mean particle diameter of 2 micrometers, 2Oaluminum3 powder with a mean particle diameter of 0.5 micrometers, Blend so that it may become the presentation which shows Mg powder with a mean particle diameter of 3 micrometers, SiO2 powder with a mean particle diameter of 4 micrometers, and B4C powder in this table, and this powder 100 weight section is received. The methyl cellulose 6 weight section, the surfactant 2.5 weight section, and the water 24 weight section were added as an organic binder, it mixed and kneaded to homogeneity, and the plastic matter for shaping was obtained. The obtained plastic matter was fabricated with the extrusion-molding machine in 0.43mm in the outer diameter of 45mm, die length of 120mm, and septum thickness, and the honeycomb configuration of a cel consistency the inch of 100cm/square (16 cels / cm2). Baking of 2 hours was performed with the burning temperature which shows this honeycomb Plastic solid in Table 1 in Ar ambient atmosphere after performing temporary quenching for cleaning at 550 degrees C in an oxidizing atmosphere for 3 hours, and the silicon carbide sintered compact of honeycomb structure was produced by porosity. About these sintered compacts, average pore size and porosity were measured in the mercury porosimeter, four more point flexural strength was measured, and the result was shown in Table 1. Moreover, when the crystal phase was identified in the X diffraction, consisting of the single phase or the compound of an oxide added as SiC and an assistant was checked.

[0047]

[Table 1]

	SiC粉末の平均粒径（μm）	SiC粉末の配合量（wt%）	Y_2O_3粉末の配合量（wt%）	MgO粉末の配合量（wt%）	Al_2O_3粉末の配合量（wt%）	SiO_2粉末の配合量（wt%）	B_4C粉末の配合量（wt%）	焼成温度（℃）	平均細孔径（μm）	気孔率（%）	4点曲げ強度（MPa）
実施例1	32.6	90	5	0	0	0	5	2000	9.5	39.6	60
実施例2	32.6	95	5	0	0	0	0	2000	10.0	42.0	52
実施例3	32.6	90	0	0	5	0	5	2000	9.0	40.1	50
実施例4	32.6	75	7	0	7	7	4	1800	10.2	45.0	48
実施例5	32.6	75	0	7	7	7	4	1800	10.6	46.1	45
実施例6	50.0	90	5	0	0	0	5	2000	13.3	44.0	55
実施例7	50.0	75	7	0	7	7	4	1800	15.0	49.0	47

[0048] (Example 8) To the powder blended so that it might become the presentation of the example 4 shown in Table 1, the silicon carbide sintered compact of honeycomb structure was produced like the example 4 except having added ZrO2 powder 1% of the weight by outside ** further. About this sintered compact, average pore size, porosity, and four-point flexural strength were measured like said examples 1-7, and that result was shown in Table 2. Moreover, when observed in the X diffraction, the halo which shows existence of a glass phase compared with an example 4 was decreasing.

[0049] (Example 9) On the occasion of baking, after holding in a maximum temperature (1800 degrees C), the silicon carbide sintered compact of honeycomb structure was produced like the example 4 except having

carried out the annealing process held at 1400 degrees C for 3 hours. About this sintered compact, average pore size, porosity, and four-point flexural strength were measured like said examples 1-7, and that result was shown in Table 2. Moreover, when observed in the X diffraction, the halo which shows existence of a glass phase compared with an example 4 was decreasing.

[0050]

[Table 2]

	平均細孔径 (μm)	気孔率 (%)	4点曲げ強度 (MPa)
実施例8	9.8	44.0	51
実施例9	10.0	44.5	52

[0051] The SiC raw material powder which has mean particle diameter as shown in Table 3, (Examples 10-12) Blend so that it may become the presentation which shows 2Oaluminum3 powder with a mean particle diameter of 0.5 micrometers, CaCO3 powder with a mean particle diameter of 0.5 micrometers, and SiO2 powder with a mean particle diameter of 4 micrometers in this table, and this powder 100 weight section is received. The methyl cellulose 6 weight section, the surfactant 2.5 weight section, and the water 24 weight section were added as an organic binder, it mixed and kneaded to homogeneity, and the plastic matter for shaping was obtained. After fabricating the obtained plastic matter in the honeycomb configuration like said examples 1-7 and performing temporary quenching for cleaning at 550 degrees C in an oxidizing atmosphere for 3 hours, baking of 2 hours was performed with the burning temperature shown in Table 3 in N2 ambient atmosphere, and the silicon carbide sintered compact of honeycomb structure was produced by porosity. About these sintered compacts, average pore size, porosity, and four-point flexural strength were measured like said examples 1-7, and the result was shown in Table 3. moreover, the place which identified the crystal phase in the X diffraction -- an example 10 -- AlN -- an example 11 -- Si3 -- in the example 12, SiAlON was identified for N4 and AlN in addition to SiC, respectively.

[0052]

[Table 3]

	SiC粉末の平均粒径（μm）	SiC粉末の配合量（wt%）	Al_2O_3粉末の配合量（wt%）	$CaCO_3$粉末の配合量（wt%）	SiO_2粉末の配合量（wt%）	焼成温度（℃）	平均細孔径（μm）	気孔率（%）	4点曲げ強度（MPa）
実施例10	32.6	88	9	8	-	1800	10.0	50.0	20
実施例11	32.6	60	10	-	30	1800	14.0	50.0	25
実施例12	32.6	60	10	-	30	1600	13.0	52.0	24

[0053]
[Effect of the Invention] As explained above, though fireproof particles, such as a silicon carbide particle, are included, since it can be made to sinter with a comparatively low burning temperature at the time of the manufacture, the honeycomb structure object of this invention can improve [a yield's] while holding down a manufacturing cost, and can be offered cheaply. Moreover, since it is a porous honeycomb structure object, it can be suitably used also under high SV conditions as a filter, catalyst support, etc. for automobile exhaust purification.

[Translation done.]

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(54)【発明の名称】　ハニカム構造体及びその製造方法

(57)【要約】
【課題】　炭化珪素粒子のような耐火性粒子を含みながらも比較的低い焼成温度で安価に製造できるとともに、十分に多孔質かつ高比表面積で、自動車排ガス浄化用のフィルターや触媒担体等として高ＳＶ条件下でも好適に使用できるハニカム構造体を提供する。
【解決手段】　隔壁により仕切られた軸方向に貫通する多数の流通孔を有するハニカム構造体であって、骨材となる耐火性粒子と、希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素とを含み、これらの元素を１種以上含有する結晶を有し、多孔質であるハニカム構造体。

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【特許請求の範囲】

【請求項１】　隔壁により仕切られた軸方向に貫通する多数の流通孔を有するハニカム構造体であって、骨材となる耐火性粒子と、希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素とを含み、これらの元素を１種以上含有する結晶を有し、多孔質であることを特徴とするハニカム構造体。

【請求項２】　更に、Ｂ及び／又はＣを含む請求項１記載のハニカム構造体。

【請求項３】　前記耐火性粒子が、その原料粒子形状を留めた状態で前記結晶により結合された構造を有する請求項１記載のハニカム構造体。

【請求項４】　前記耐火性粒子が、炭化珪素粒子である請求項１記載のハニカム構造体。

【請求項５】　含塵流体中に含まれる粒子状物質を捕集除去するフィルターとして用いられる請求項１記載のハニカム構造体。

【請求項６】　気孔率が３０～９０％の範囲にある請求項１記載のハニカム構造体。

【請求項７】　平均細孔径が２～５０μｍの範囲にある請求項１記載のハニカム構造体。

【請求項８】　前記隔壁の厚さが１０２～１２７０μｍである請求項１記載のハニカム構造体。

【請求項９】　前記隔壁の厚さとハニカム構造体の気孔率とが以下の関係を満たす請求項１記載のハニカム構造体。

【数１】隔壁の厚さ(μｍ)≧気孔率(%)×４

【請求項１０】　前記隔壁の厚さとハニカム構造体の気孔率とが以下の関係を満たす請求項１記載のハニカム構造体。

【数２】隔壁の厚さ(μｍ)≧気孔率(%)×５

【請求項１１】　前記隔壁の厚さとハニカム構造体の気孔率とが以下の関係を満たす請求項１記載のハニカム構造体。

【数３】隔壁の厚さ(μｍ)≦気孔率(%)×２０

【請求項１２】　セル密度が０．７～１５５セル／ｃｍ²である請求項１記載のハニカム構造体。

【請求項１３】　耐火性粒子原料に、希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料と有機バインダーとを添加し混合及び混練して得られた坏土をハニカム形状に成形し、得られた成形体を仮焼して成形体中の有機バインダーを除去した後、本焼成することを特徴とするハニカム構造体の製造方法。

【請求項１４】　前記耐火性粒子原料が、炭化珪素粒子原料である請求項１３記載の製造方法。

【請求項１５】　前記耐火性粒子原料の平均粒径が、最終的に得られるハニカム構造体の平均細孔径の２～４倍である請求項１３記載の製造方法。

【請求項１６】　前記希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料の添加量が、耐火性粒子の表面積に対し３～３０ｇ／ｍ²である請求項１３記載の製造方法。

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【請求項１７】　前記アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料の平均粒径が、骨材である耐火性粒子の平均粒径の５０％以下である請求項１３記載の製造方法。

【請求項１８】　前記有機バインダーを、前記耐火性粒子原料と希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料との合計量に対して、外配で２～３０重量%の範囲で添加する請求項１３記載の製造方法。

【請求項１９】　前記坏土を調合する際に、造孔剤を、前記耐火性粒子原料と希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料との合計量に対して、外配で３０重量%以下の範囲で添加する請求項１３記載の製造方法。

【請求項２０】　前記坏土を調合する際に、前記耐火性粒子原料に、更にＢ及び／又はＣを含む原料を添加する請求項１３記載の製造方法。

【請求項２１】　前記坏土を調合する際に、前記耐火性粒子原料に、更に核生成剤として４価以上の元素を添加する請求項１３記載の製造方法。

【請求項２２】　前記成形体の仮焼を、前記希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料が溶融する温度より低い温度にて実施する請求項１３記載の製造方法。

【請求項２３】　前記本焼成を、１５００～２０００℃の温度範囲で実施する請求項１３記載の製造方法。

【請求項２４】　前記本焼成において、最高焼成温度で保持した後、１５００℃以下の温度で保持する結晶化のためのアニール工程を設ける請求項１３記載の製造方法。

【発明の詳細な説明】

【０００１】

【発明の属する技術分野】　本発明は、自動車排ガス浄化用のフィルターや触媒担体等に使用されるハニカム構造体に関する。

【０００２】

【従来の技術】　ディーゼルエンジン排ガスのような含塵流体中に含まれる粒子状物質を捕集除去するためのフィルター、あるいは排ガス中の有害物質を浄化する触媒成分を担持するための触媒担体として、多孔質のハニカム構造体が広く使用されている。また、このようなハニカム構造体の構成材料として、炭化珪素（ＳｉＣ）粒子のような耐火性粒子を使用することが知られている。

【０００３】　具体的な関連技術として、例えば特開平６－１８２２２８号公報には、所定の比表面積と不純物含有量を有する炭化珪素粉末を出発原料とし、これを所望の形状に成形、乾燥後、１６００～２２００℃の温度

範囲で焼成して得られるハニカム構造の多孔質炭化珪素質触媒担体が開示されている。

【０００４】　一方、特開昭６１－２６５５０号公報には、易酸化性素材、又は易酸化性素材を含有する耐火組成物にガラス化素材を添加し、結合材と共に混合、混練及び成形し、成形した成形体を非酸化雰囲気の炉内で焼成することを特徴とするガラス化素材含有耐火物の製造方法が、特開平８－１６５１７１号公報には、炭化珪素粉末に、有機バインダーと、粘土鉱物系、ガラス系、珪酸リチウム系の無機バインダーを添加して成形する炭化珪素成形体が、それぞれ開示されている。

【０００５】　また、前記特開平６－１８２２２８号公報には、従来の多孔質炭化珪素質焼結体の製造方法として、骨材となる炭化珪素粒子にガラス質フラックス、あるいは粘土質などの結合材を加え成形した後、その成形体を前記結合材が溶融する温度で焼き固めて製造する方法も紹介されている。

【０００６】　更に、特公昭６１－１３８４５号公報及び特公昭６１－１３８４６号公報には、珪砂、陶磁器粉砕物、Al_2O_3、TiO_2、ZrO_2等の金属酸化物、炭化珪素、窒化物、硼化物あるいはその他の耐火性材料等よりなる所定粒度に整粒された耐火性粒子が、水ガラス、フリット、釉薬等の耐火性結合材で多孔質の有底筒状体に形成された高温用セラミックフィルターについて、その好適な耐火性粒子平均径、耐火性粒子粒度分布、筒状体気孔率、筒状体平均細孔径、筒状体細孔容積、筒状体隔壁肉厚等が開示されている。

【０００７】　更にまた、特開平１０－２９８６６号公報、特開平２－６３７１号公報及び特開昭６１－９７１６５号公報には、ＳｉとＡｌの酸窒化物であるサイアロンで結合された炭化珪素質れんがの製造方法、組成等が開示されている。

【０００８】

【発明が解決しようとする課題】　前記特開平６－１８２２２８号公報に示される、炭化珪素粉末自体の再結晶反応による焼結形態（ネッキング）では、炭化珪素粒子表面から炭化珪素成分が蒸発し、これが粒子間の接触部（ネック部）に凝縮することで、ネック部が成長し結合状態が得られるが、炭化珪素を蒸発させるには、非常に高い焼成温度が必要であるため、これがコスト高を招き、かつ、熱膨張率の高い材料を高温焼成しなければならないために、焼成歩留が低下するという問題があった。

【０００９】　一方、特開昭６１－２６５５０号公報や特開平６－１８２２２８号公報に示される、原料炭化珪素粉末をガラス質で結合させる手法は、焼成温度としては１０００～１４００℃と低くて済むが、この時、結合材が一旦溶融状態となるため、多孔質体を得ることが非常に困難であった。

【００１０】　更に、特公昭６１－１３８４５号公報及び特公昭６１－１３８４６号公報に示されるフィルターは、多孔質ではあるものの、隔壁が５～２０ｍｍと厚い有底筒状体であり、自動車排ガス浄化用フィルターのような高ＳＶ（空間速度）条件下には適用できなかった。

【００１１】　更にまた、特開平１０－２９８６６号公報、特開平２－６３７１号公報及び特開昭６１－９７１６５号公報に示されるサイアロンで結合された炭化珪素質れんがは、いずれも炉の内張り、棚板などに用いられるもので、気孔率が２０％以下と小さく、圧力損失を考慮すると自動車排ガス浄化用フィルターのような用途には全く適さないものであった。

【００１２】　本発明は、このような従来の事情に鑑みてなされたものであり、炭化珪素粒子のような耐火性粒子を含みながらも比較的低い焼成温度で安価に製造できるとともに、十分に多孔質かつ高比表面積で、目封じ等の処理により自動車排ガス浄化用のフィルターとして、あるいは触媒担体等として高ＳＶ条件下でも好適に使用できるハニカム構造体とその製造方法を提供することを目的とする。

【００１３】

【課題を解決するための手段】　本発明によれば、隔壁により仕切られた軸方向に貫通する多数の流通孔を有するハニカム構造体であって、骨材となる耐火性粒子と、希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素とを含み、これらの元素を１種以上含有する結晶を有し、多孔質であることを特徴とするハニカム構造体、が提供される。

【００１４】　また、本発明によれば、耐火性粒子原料に、希土類、アルカリ土類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料と有機バインダーとを添加し混合及び混練して得られた坏土をハニカム形状に成形し、得られた成形体を仮焼して成形体中の有機バインダーを除去した後、本焼成することを特徴とするハニカム構造体の製造方法、が提供される。

【００１５】

【発明の実施の形態】　本発明のハニカム構造体は、例えば前記特開平６－１８２２２８号公報に記載された製造方法が、焼結機構の中で蒸発凝縮という機構を利用しているのに対し、溶解析出という機構を利用して耐火性粒子同士を結合させたものである。この溶解析出機構では、適当な焼結助剤を選択し、骨材である耐火性粒子に添加、混合して焼成すると、その助剤が耐火性粒子と反応し、その際に耐火性粒子の表面が溶解して液相を生成する。溶解した成分は、添加した助剤の成分を含んだまま、液相の状態でエネルギー状態の低いネック部に移動して析出し、ネック部に移動した物質が粒子同士を結合させる。

【００１６】　液相は、焼成過程の中でまず最初に助剤同士が反応して液相を生成してそれが耐火性粒子と反応

することもあれば、助剤と耐火性粒子の反応によって生成する場合もある。ただし、一般には液相の状態の方が耐火性粒子には濡れ易く、反応が容易になるため、助剤同士が焼成温度より低い共晶点を有する組み合わせを選択することが好ましい。具体的には、助剤として、希土類（Ｙ、Ｌａ、Ｃｅ、Ｙｂ等）、アルカリ土類（Ｍｇ、Ｃａ、Ｓｒ、Ｂａ等）、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素を含んだ１種以上の原料（以下、「希土類等含有原料」という。）を使用する。前記元素の内でも、特にＳｉは助剤の融点を下げるのに効果的である。

【００１７】　本発明のハニカム構造体に含まれる、希土類、アルカリ度類、Ａｌ及びＳｉからなる群より選ばれた１種以上の元素は、このように、その製造時に助剤として添加された原料に含まれていたものであり、主にネック部で析出した結晶に含有されて構造体中に存在している。更に、耐火性粒子には粒子表面の物質移動を促進する元素としてＢ及び／又はＣを含む原料、例えばこれらの化合物であるB_4Cを添加してもよく、この場合、得られたハニカム構造体にはＢ及び／又はＣも含まれることになる。

【００１８】　また、本発明のハニカム構造体は、助剤として添加した原料に含まれる前記の元素を１種以上含有する結晶を有するが、これはすなわち、液相から結晶が析出したことを意味している。前記のように骨材となる耐火性粒子の結合に液相を利用する以上、液相から結晶が析出しなければ焼成体中にガラスとして残存してしまうことになるが、ガラスがネック部の主たる相になってしまうと、耐火性粒子のネック部における強度、耐蝕性、耐熱性が十分でなくなるため、ハニカム構造体そのものの特性が低下してしまう。このため、液相からは結晶が析出している必要がある。

【００１９】　以上のように、本発明のハニカム構造体は、再結晶法のように耐火性粒子そのものを蒸発させるのではなく、反応及びこれに伴ない生成する液相を利用して耐火性粒子を結合していることから、その焼成時おいてあまり高い温度を必要とせず、製造コストを抑えるとともに歩留を向上させることができる。また、本発明は、特公昭６１－１３８４５号公報や特公昭６１－１３８４６号公報に示されるような厚壁の有底筒状体でも、特開平１０－２９８６６号公報、特開平２－６３７１号公報及び特開昭６１－９７１６５号公報に示されるようなれんがでもなく、多孔質のハニカム構造体であるので、自動車排ガス浄化用のフィルターや触媒担体等として高ＳＶ条件下で使用できる。

【００２０】　本発明のハニカム構造体は、その微構造として、耐火性粒子が、その原料粒子形状を留めた状態で結晶により結合された構造を有することが好ましい。また、本発明のハニカム構造体を、含塵流体中に含まれる粒子状物質を捕集除去するためのフィルターとして用いる場合には、その気孔率を３０～９０％の範囲とすることが好ましい。ハニカム構造体の気孔率が３０％未満では濾過速度が不足し、９０％を超えると構造体としての強度が不足する。更に、自動車排ガス浄化用フィルター等の圧力損失が懸念される用途に用いる場合には、気孔率を４０％以上とすることが好ましい。

【００２１】　同様に本発明のハニカム構造体をフィルターとして用いる場合、ハニカム構造体の平均細孔径は、濾過する対象に応じて決定することが好ましい。例えば、ディーゼルエンジンから排出される排気ガス中に含まれるパティキュレートを捕集除去するためのディーゼルパティキュレートフィルター（ＤＰＦ）として用いる場合には、平均細孔径を２～５０μｍの範囲とすることが好ましい。平均細孔径が２μｍ未満ではパティキュレートの少量堆積によっても著しく圧損が上昇し、逆に、平均細孔径が５０μｍを超えるとパティキュレートの素抜けが起こるため、好ましくない。

【００２２】　ハニカム構造体の流通孔（セル）を仕切る隔壁の厚さは、４ｍｉｌ以上（１０２μｍ以上）とすることが好ましい。隔壁の厚さが４ｍｉｌ（１０２μｍ）未満では、構造体として十分な強度を維持することが困難となる。また、強度は気孔率と密接な関係にあり、本発明のハニカム構造体の場合、隔壁の厚さと気孔率とが以下の関係を満たすように隔壁の厚さを設定すれば、必要な強度が得られ、好ましいことが判明した。

【数４】隔壁の厚さ(μｍ)≧気孔率(%)×４

【００２３】　更に、隔壁の厚さと気孔率とが以下の関係を満たすように隔壁の厚さを設定すれば、十分な強度が得られるため、より好ましい。

【数５】隔壁の厚さ(μｍ)≧気孔率(%)×５

【００２４】　一方で、ＤＰＦ等のフィルターとして用いる場合には、隔壁の厚さを、５０ｍｉｌ以下（１２７０μｍ以下）とすることが好ましい。隔壁の厚さが５０ｍｉｌ（１２７０μｍ）を超えると、濾過速度不足や圧損上昇が懸念されるためである。なお、これについても気孔率と密接な関係があり、隔壁の厚さと気孔率とが以下の関係を満たすように隔壁の厚さを設定することによって、問題を回避することができる。

【数６】隔壁の厚さ(μｍ)≦気孔率(%)×２０

【００２５】　ハニカム構造体のセル密度は、５～１０００セル／平方インチ（０．７～１５５セル／cm^2）の範囲とすることが好ましい。セル密度が５セル／平方インチ（０．７セル／cm^2）未満では、ハニカム構造体として強度不足となるとともに、フィルターとして用いた場合には、濾過面積も不足する。逆に、１０００セル／平方インチ（１５５セル／cm^2）を超えると圧損上昇を招くため、好ましくない。

【００２６】　次に、本発明のハニカム構造体の製造方法について説明する。本発明のハニカム構造体を製造するにあたっては、まず、耐火性粒子原料に希土類等含有

原料と有機バインダーとを添加して混合及び混練し、成形用の坏土を得る。

【００２７】　使用する耐火性粒子の種類は特に限定されないが、酸化物系ではAl_2O_3、ZrO_2、Y_2O_3、炭化物系ではＳｉＣ、窒化物系ではSi_3N_4、ＡｌＮ、その他ムライト等の粒子が好適に用いられ、例えば、蓄積したパティキュレートを燃焼処理する際にしばしば高温に晒されるＤＰＦ等の用途には、ＳｉＣ等が耐熱性が高く、好適に用いられる。

【００２８】　耐火性粒子原料の平均粒径は、本製造方法にて最終的に得られるハニカム構造体（焼結体）の平均細孔径の２～４倍であることが好ましい。本製造方法で得られるハニカム構造体は、焼成温度が比較的低いために耐火性粒子原料の粒子形状や粒径が概ね焼成後まで維持される。したがって、前記比率が２倍未満であると、所望の細孔径に対して粒径が小さ過ぎ、結果的に、小さな耐火性粒子群が析出した結晶で細長く結合されて大きな細孔を形成することになり、ハニカム構造体のような薄壁の構造体を維持し得る程高い強度を得ることが困難である。

【００２９】　また、例えば耐火性粒子がＳｉＣ粒子の場合、従来多孔質ハニカム構造体に適用されてきた再結晶ＳｉＣが、その反応機構から、所望とする細孔径とほぼ同等の骨材原料粒径を必要とするのに対し、本発明のハニカム構造体のように析出した結晶により結合されたＳｉＣ粒子は、粒径が細孔径の２倍以上でよいので、同じ細孔径を得ようとした時に、再結晶ＳｉＣに比べて粗い、すなわち安価な原料を使用することができ、コストメリットも大きい。

【００３０】　逆に、前記比率が４倍を超える場合には、所望の細孔径に対して用いる耐火性粒子の粒径が大き過ぎ、成形の段階で耐火性粒子を密に充填することによっても、その間隙に所望の細孔を得ることが困難となり、更にフィルター用途では、気孔率低下を招く点でも好ましくない。

【００３１】　希土類等含有原料は、焼成中に耐火性粒子と反応し、あるいは当該原料同士で反応して、液相を生成し、それが耐火性粒子にまとわりつき粒子同士を接合する役割を担うため、その適切な添加量は、耐火性粒子の表面積と密接な関わりがある。そして、この場合の耐火性粒子の表面積とは、液相が耐火性粒子を覆い接着することを論じている訳であるから、粒子の形状等にもよるが、一般的には、いわゆるＢＥＴ比表面積よりむしろ耐火性粒子を球体とみなした幾何学的表面積$S=4\pi r^2$（ｒは耐火性粒子の平均粒径）を用いる方が適切である。この幾何学的表面積$S=4\pi r^2$を用いると、「耐火性粒子単位表面積当たりの希土類等含有原料の量Ｗ」を、下式にて簡易的に算出することができる。

【数７】$W=\{(4/3\pi r^3\times\rho)/(\text{耐火性粒子の重量割合})\}\times\{(\text{希土類等含有原料の重量割合})/(4\pi r^2)\}$

（ここで、ｒは耐火性粒子の平均粒径、ρは耐火性粒子の比重である。）

【００３２】　本発明の製造方法において、希土類等含有原料の添加量は、「耐火性粒子単位表面積当たりの希土類等含有原料の量Ｗ」が、３～３０ｇ／ｍ²となるように設定することが好ましい。３ｇ／ｍ²未満では、結合材が不足して、ハニカム構造のような薄壁の構造体を維持し得る強度を得ることが難しく、逆に３０ｇ／ｍ²を超えると、適切に耐火性粒子同士を結合し得る以上に過剰に液相が生成されるため、強度は向上するものの、気孔率低下、平均細孔径縮小などの弊害が併発してくる。

【００３３】　希土類等含有原料の平均粒径は、骨材である耐火性粒子の平均粒径の５０％以下であることが好ましい。希土類等含有原料は焼成で液相を生成し、集合しながら耐火性粒子にまとわりつくように移動するため、その粒径が耐火性粒子の粒径の５０％を超えると、成形時に希土類等含有原料の粒子が占有していた空間が大きな空隙となって残り、強度低下を招いたり、フィルターとして使用する場合にはフィルター効率低下（濾過漏れ）の原因となったりする。

【００３４】　また、一般に、ハニカム構造体の押出成形時には、ある程度粒度差のある２種以上の原料粉末を混合する方が滑らかに押し出すことができ、その観点からは、希土類等含有原料の平均粒径を、骨材である耐火性粒子の平均粒径の３０％以下にすることが好ましい。希土類等含有原料の原料形態としては、通常、酸化物を用いるが、必要により硝酸塩や塩化物のような無機塩、窒化物、金属なども使用できる。また必要元素のうち２種以上を含んだ化合物、例えば粘土鉱物などを用いると、コストや、成形性を良くすることによる生産性の向上などの点で有利になる。

【００３５】　耐火性粒子を骨材とし、希土類等含有原料及び必要に応じて造孔剤等を配合してなる坏土を、ハニカム形状に滑らかに押出成形するため、成形助剤として、１種以上の有機バインダーを、主原料（耐火性粒子原料と希土類等含有原料）の合計量に対し外配で２重量％以上添加することが好ましい。ただし、３０重量％を超える添加は、仮焼後に過剰な高気孔率を招き、強度不足に至らしめるため好ましくない。

【００３６】　更に、隔壁の厚さが２０ｍｉｌ（５０８μｍ）以下のハニカム構造体に押出成形する場合には、有機バインダーを４～２０重量％の範囲で添加することが好ましい。添加量が４重量％未満では斯様な薄壁に押出すことが難しく、逆に、２０重量％を超えると、押出し後にその形状を維持することが困難となる。

【００３７】　ハニカム構造体をフィルターとして使用する場合には、気孔率を高める目的で、坏土の調合時に造孔剤を添加してもよい。造孔剤の添加量は、主原料（耐火性粒子原料と希土類等含有原料）の合計量に対

し、外配で３０重量%以下とすることが好ましい。添加量が３０重量%を超えると、過度に気孔率が高くなり強度不足に至る。造孔剤は、それが燃焼して抜けた跡に気孔が形成されるため、その平均粒径が焼成後に得ようとする平均細孔径に対し、２５～１００%の範囲であることが好ましい。使用する造孔剤としては、例えば、グラファイト、小麦粉、澱粉、フェノール樹脂、ポリメタクリル酸メチル、ポリエチレン、ポリエチレンテレフタレート等を挙げることができる。造孔剤は、目的に応じて１種を単独で使用してもよいし、２種以上を組み合わせて使用してもよい。

【００３８】　また、本発明の製造方法においては、前述のように液相から結晶が析出する必要があるが、この結晶化を促進するために、耐火性粒子原料に、核生成剤として４価以上の元素（Ｚｒ、Ｔａ、Ｔｉ、Ｐ等）を添加するようにしてもよい。更にまた、耐火性粒子原料には、粒子表面の物質移動を促進する元素であるＢ及び／又はＣを含む原料を添加してもよい。

【００３９】　前記原料を常法により混合及び混練して得られた坏土を、押出成形法等により所望のハニカム形状に成形する。次いで、得られた成形体を仮焼して成形体中に含まれる有機バインダーを除去（脱脂）した後、本焼成を行う。仮焼は、希土類等含有原料が溶融する温度より低い温度にて実施することが好ましい。具体的には、１５０～７００℃程度の所定の温度で一旦保持してもよく、また、所定温度域で昇温速度を５０℃／ｈｒ以下に遅くして仮焼してもよい。

【００４０】　所定の温度で一旦保持する手法については、使用した有機バインダーの種類と量により、一温度水準のみの保持でも複数温度水準での保持でもよく、更に複数温度水準で保持する場合には、互いに保持時間を同じにしても異ならせてもよい。また、昇温速度を遅くする手法についても同様に、ある一温度区域間のみ遅くしても複数区間で遅くしてもよく、更に複数区間の場合には、互いに速度を同じとしても異ならせてもよい。

【００４１】　仮焼の雰囲気については、酸化雰囲気でもよいが、成形体中に有機バインダーが多く含まれる場合には、仮焼中にそれ等が酸素で激しく燃焼して成形体温度を急激に上昇せしめることがあるため、N_2、Ａｒ等の不活性雰囲気で行うことによって、成形体の異常昇温を抑制することも好ましい手法である。この異常昇温の抑制は、熱膨張係数の大きい（熱衝撃に弱い）原料を用いた場合に重要な制御である。有機バインダーを、例えば主原料に対して２０重量%（外配）以上添加した場合には、前記不活性雰囲気にて仮焼するのが好ましい。

【００４２】　仮焼とそれに続く本焼成は、同一のあるいは別個の炉にて、別工程として行ってもよく、また、同一炉での連続工程としてもよい。仮焼と本焼成を異なる雰囲気にて実施する場合には前者も好ましい手法であるが、総焼成時間、炉の運転コスト等の見地からは後者の手法も好ましい。

【００４３】　本焼成の温度は、用いる希土類等含有原料によって異なるが、通常１５００～２０００℃の範囲で実施することが好ましい。本焼成の実施温度が１５００℃未満では、液相が十分に生成されないため耐火性粒子同士が強固に結合されず、逆に、１６００℃を超えると、溶解した成分の粘性が低下し過ぎて焼成体表面近傍や焼成体下部に集中する等の偏りが生じるため好ましくない。なお、この本焼成においては、結晶化を促進する目的で、最高温度に保持した後、１５００℃以下の温度で保持する結晶化のためのアニール工程を設けることが好ましい。

【００４４】　また、本焼成の雰囲気については、耐火性粒子の種類によって選択することが好ましく、例えば、耐火性粒子が耐酸化性を有する場合には酸化雰囲気での焼成も可能であるが、ＳｉＣをはじめとする炭化物の粒子、Si_3N_4、ＡｌＮに代表される窒化物の粒子等、高温での酸化が懸念されるものについては、少なくとも酸化が始まる温度以上の温度域においては、N_2、Ａｒ等の非酸化雰囲気とすることが好ましい。なお、N_2雰囲気で焼成する場合には、結合材の結晶相が窒化物や酸窒化物になり、強度や熱伝導率において結晶相を酸化物とするよりも良い特性が得られることがあるので、目的に応じて焼成雰囲気を使い分けていくことも好ましい。

【００４５】

【実施例】　以下、本発明を実施例に基づいて更に詳細に説明するが、本発明はこれらの実施例に限定されるものではない。

【００４６】（実施例１～７）表１に示すような平均粒径を有するＳｉＣ原料粉末、平均粒径２μｍのY_2O_3粉末、平均粒径０．５μｍのAl_2O_3粉末、平均粒径３μｍのＭｇ粉末、平均粒径４μｍのSiO_2粉末、及びＢ，Ｃ粉末を、同表に示す組成となるように配合し、この粉末１００重量部に対して、有機バインダーとしてメチルセルロース６重量部、界面活性剤２．５重量部、及び水２４重量部を加え、均一に混合及び混練して成形用の坏土を得た。得られた坏土を、押出し成形機にて外径４５ｍｍ、長さ１２０ｍｍ、隔壁厚さ０．４３ｍｍ、セル密度１００セン千／平方インチ（１６セル／cm^2）のハニカム形状に成形した。このハニカム成形体を酸化雰囲気において５５０℃で３時間、脱脂のための仮焼を行った後、Ａｒ雰囲気において表１に示す焼成温度にて２時間の焼成を行い、多孔質でハニカム構造の炭化珪素焼結体を作製した。これらの焼結体について、水銀ポロシメーターにて平均細孔径と気孔率を測定し、更に４点曲げ強度を測定して、その結果を表１に示した。また、Ｘ線回折にて結晶相を同定したところ、ＳｉＣ及び助剤として添加した酸化物の単相又は化合物からなっていることが確認された。

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【００４７】
【表１】

	SiC粉末の平均粒径（μm）	SiC粉末の配合量（wt%）	Y_2O_3粉末の配合量（wt%）	MgO粉末の配合量（wt%）	Al_2O_3粉末の配合量（wt%）	SiO_2粉末の配合量（wt%）	B_4C粉末の配合量（wt%）	焼成温度（℃）	平均細孔径（μm）	気孔率（%）	４点曲げ強度（MPa）
実施例１	32.6	90	5	0	0	0	5	2000	9.5	39.6	60
実施例２	32.6	95	5	0	0	0	0	2000	10.0	42.0	52
実施例３	32.6	90	0	0	5	0	5	2000	9.0	40.1	50
実施例４	32.6	75	7	0	7	7	4	1800	10.2	46.0	48
実施例５	32.6	75	0	7	7	7	4	1800	10.6	46.1	45
実施例６	50.0	90	5	0	0	0	5	2000	13.3	44.0	55
実施例７	50.0	75	7	0	7	7	4	1800	15.0	49.0	47

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＊【００４８】（実施例８）表１に示す実施例４の組成となるように配合した粉末に、更に外配でZrO_2粉末を１重量%添加した以外は、実施例４と同様にしてハニカム構造の炭化珪素焼結体を作製した。この焼結体について、前記実施例１～７と同様に平均細孔径、気孔率、及び４点曲げ強度を測定し、その結果を表２に示した。また、X線回折にて観察したところ、実施例４に比べてガラス相の存在を示すハローが減少していた。

【００４９】（実施例９）焼成の際に、最高温度（１８００℃）にて保持した後、１４００℃で３時間保持するアニール工程を実施した以外は、実施例４と同様にしてハニカム構造の炭化珪素焼結体を作製した。この焼結体について、前記実施例１～７と同様に平均細孔径、気孔率、及び４点曲げ強度を測定し、その結果を表２に示した。また、X線回折にて観察したところ、実施例４に比べてガラス相の存在を示すハローが減少していた。

【００５０】
【表２】

＊

	平均細孔径（μm）	気孔率（%）	４点曲げ強度（MPa）
実施例８	9.8	44.0	51
実施例９	10.0	44.5	52

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【００５１】（実施例１０～１２）表３に示すような平均粒径を有するＳｉＣ原料粉末、平均粒径０．５μｍのＡｌ$_2$Ｏ$_3$粉末、平均粒径０．５μｍのＣａＣＯ$_3$粉末、平均粒径４μｍのＳｉＯ$_2$粉末を、同表に示す組成となるように配合し、この粉末１００重量部に対して、有機バインダーとしてメチルセルロース６重量部、界面活性剤２．５重量部、及び水２４重量部を加え、均一に混合及び混練して成形用の坏土を得た。得られた坏土を前記実施例１～７と同様にしてハニカム形状に成形し、酸化雰囲気において５５０℃で３時間、脱脂のための仮焼を行った後、Ｎ$_2$雰囲気において表３に示す焼成温度にて２時間の焼成を行い、多孔質でハニカム構造の炭化珪素焼結体を作製した。これらの焼結体について、前記実施例１～７と同様に平均細孔径、気孔率、及び４点曲げ強度を測定し、その結果を表３に示した。また、Ｘ線回折にて結晶相を同定したところ、実施例１０ではＡｌＮが、実施例１１ではＳｉ$_3$Ｎ$_4$とＡｌＮが、実施例１２ではＳｉＡｌＯＮが、それぞれＳｉＣ以外に同定された。

【００５２】

【表３】

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	SiC粉末の平均粒径（μm）	SiC粉末の配合量（wt%）	Al_2O_3粉末の配合量（wt%）	$CaCO_3$粉末の配合量（wt%）	SiO_2粉末の配合量（wt%）	焼成温度（℃）	平均細孔径（μm）	気孔率（%）	4点曲げ強度（MPa）
実施例10	32.6	88	9	8	-	1800	10.0	50.0	20
実施例11	32.6	60	10	-	30	1800	14.0	50.0	25
実施例12	32.6	60	10	-	30	1600	13.0	52.0	24

【００５３】

【発明の効果】　以上説明したように、本発明のハニカム構造体は、炭化珪素粒子等の耐火性粒子を含みながらも、その製造時において比較的低い焼成温度で焼結させることができるので、製造コストを抑えるとともに歩留も向上し、安価に提供することができる。また、多孔質のハニカム構造体であるので、自動車排ガス浄化用のフィルターや触媒担体等として高ＳＶ条件下でも好適に使用できる。

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